VOL. XXIX JULY, 1913 No. 1

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OF THE

ELISHA MITCHELL SCIENTIFIC SOCIETY

ISSUED QUARTERLY

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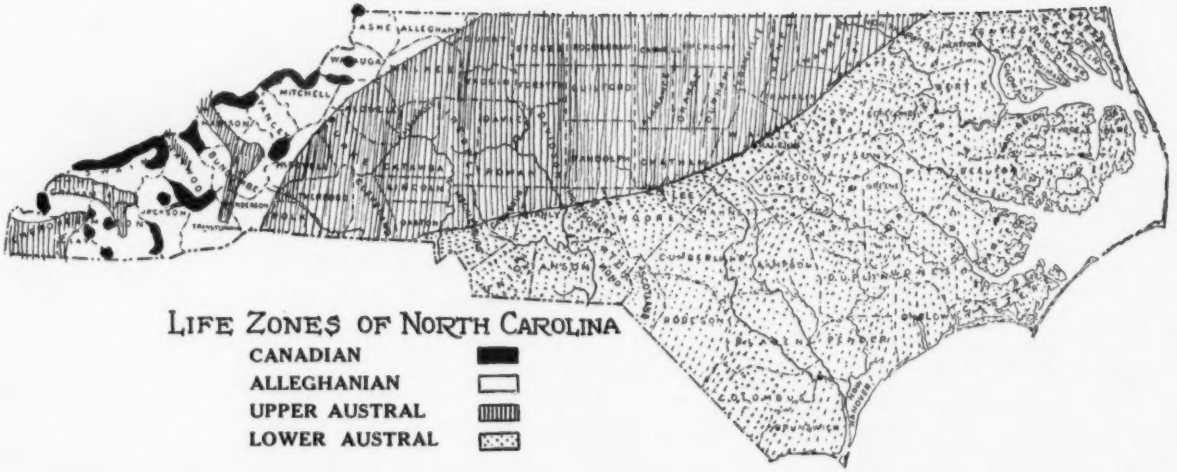

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JOURNAL
OF THE
ELISHA MITCHELL SCIENTIFIC SOCIETY

VOLUME XXIX JULY, 1913 No. 1

PROCEEDINGS OF THE TWELFTH ANNUAL MEETING OF THE NORTH CAROLINA ACADEMY OF SCIENCE HELD AT THE STATE NORMAL AND INDUSTRIAL COLLEGE, GREENSBORO, N. C., FRIDAY AND SATURDAY, APRIL 25-26, 1913.

The Executive Committee met at 2:40 P. M. Friday, April 26. There were present C. S. Brimley, President, and E. W. Gudger, Secretary *ex officio,* and by appointment in the absence of the other regular members, Dr. H. V. Wilson and Prof. C. W. Edwards. The Secretary made his report as to the state of finances and membership which was referred to the academy. An invitation of the faculty of Trinity College, Durham, to hold the next annual meeting there, was accepted. The following were elected to membership:

Briggs, R. W., Professor of Engineering, Trinity College.
Cunningham, Bert, Instructor in Sciences, High School, Durham.
Dixon, Alfred A., Professor of Physics, Guilford College.
Downing, John S., Professor of Chemistry, Guilford College.
George, W. C., Instructor in Zoology, University of North Carolina.
Metcalf, C. L., State Department of Agriculture, Raleigh.
Radcliffe, Lewis, Director, Laboratory of United States Bureau of Fisheries, Beaufort.
Ragsdale, Virginia, Associate Professor of Mathematics, StateNormal College.
Rosenkrans, D. B., Instructor in Botany, Agriculture and Mechanical College, West Raleigh.
Smith, John E., Instructor in Geology, University of North Carolina.
Swarthout, G. E., Professor of Natural Science, Atlantic Christian College, Wilson.
Winters, R. Y., Plant Breeder, North Carolina Agriculture Experiment Station.

The Secretary then read the following letters together with his reply thereto:

Dr. E. W. Gudger,
Secretary, North Carolina Academy of Science,
Greensboro, N. C.

DEAR SIR:—

You are doubtless aware that the Ninth International Zoological Congress is to be held in Monaco, March 25th to 29th 1913. I am to attend the Congress as an official delegate and will sail from New York on March 1st.

If the North Carolina Academy wishes to be represented at this Congress without expense to the Academy, I can act in this capacity should you so desire.

Respectfully,
C. W. STILES.

Dr. C. W. Stiles,
United States Public Health Service,
Washington, D. C.

DEAR SIR:—

You are hereby appointed the official representative of the North Carolina Academy of Science at the Ninth International Zoological Congress to be held at Monaco, March 25-29, 1913. This letter will constitute your credentials to the authorities of the Congress.

Very truly yours,
E. W. GUDGER, *Secretary.*

These were ordered transmitted to the Academy that they might be recorded in the proceedings. There being no further business, the Committee adjourned.

President Brimley called the Academy to order at 3 P. M., 14 members being present, and appointed the following committees:

Auditing—Coker, W. C., Wolfe, J. J., Metcalf, Z. P.

Resolutions—Hutt, W. N., George, W. C., Swarthout, G. E.

Nominations—Edwards, C. W., Wilson, H. V., Binford, Raymond.

The reading and discussion of papers was then begun and continued until adjournment at 5:45 when eight had been read.

At 8:30 P. M. the Academy reassembled in the Physics Lecture Room of the McIver Memorial Building, when, after a cordial address of welcome to the College by President J. I. Foust, President C. S. Brimley of the Academy, delivered his

presidential address on "Zoo-Geography." The Academy then adjourned to the reception hall of the Students' Building, where a reception in their honor was given by the Faculty of the College.

The Academy met in annual business session at 9:20 A. M. Saturday with President Brimley in the chair. The minutes of last meeting were read and approved, and reports of the Secretary and of committees were called for.

The Secretary read an invitation from the Greensboro Country Club, extending to the members of the Academy the courtesies of the Club during their stay in Greensboro. He then reported that on Jan. 1, 1912, the membership of the Academy was 85, that 10 members were lost through resignation, removal from the State, or non-payment of dues, but that 5 new members were elected at the 1912 meeting, making a total for 1912 of 80. By vote of the Academy the Secretary was instructed to confer with the Editor of the MITCHELL JOURNAL to see if it would not be possible to publish in the Proceedings every May a list of the members for the current year.

The Secretary then reported for the Executive Committee its action of yesterday as to membership and place of next meeting. The Nominating Committee offered for officers for 1913-14: President, Franklin Sherman, Jr., State Entomologist; Vice-president, Z. P. Metcalf, Professor of Entomology, Agricultural and Mechanical College; Secretary-Treasurer, E. W. Gudger, Professor of Biology and Geology State Normal College; for additional members of Executive Committee, W. C. Coker, Professor of Botany, University of N. C.; J. J. Wolfe, Professor of Biology and Geology, Trinity College; C. S. Brimley, Naturalist, Raleigh.

The Auditing Committee announced that the Treasurer's report as given below is correct. It was read and ordered printed in the Proceedings:

REPORT OF E. W. GUDGER, TREASURER, 1912-13, APRIL 21, 1913

RECEIPTS

Balance last audit	$193.00
Dues since last audit	84.00
Interest Savings Bank	5.08
Receipts total	$282.08
Expenses total	91.96
Balance total	$190.12

RESOURCES

Savings bank balance	$130.76
Checking bank balance	59.36
Total	$190.12
Dues unpaid (about)	25.00
Stamped Envelopes on hand	1.50
	$216.12
Less outstanding debts	83.00
Estimated Balance	$133.12

EXPENSES

Printing	$ 8.87
Postage	3.14
Typewriting	1.15
Secretary's expenses 1912 meeting	3.80
Proceedings 1912	75.00
Expenses total	$ 91.96

OUTSTANDING DEBTS

Proceedings 1913	$ 75.00
Miscellaneous (about)	8.00
Total	$ 83.00

Note transfer of $13.00 from Savings Bank to Checking Account.

The Committee on Resolutions moved a vote of thanks to the Faculty of the State Normal College for the use of rooms, and for the reception tendered its members; to the press of the city for the excellent manner in which the meeting had been reported, and to the Country Club for its invitation.

The Committee appointed in 1912 to bring in a report with recommendations for laws on ventilation of churches, school

houses, theaters, and other public buildings, was called for. Chairman Edwards reported progress and asked for further time, and on motion was instructed to bring in a report at the 1914 meeting.

At 9:40 A. M., the reading and discussion of papers was resumed and continued until the program was finished when adjournment was had at 1:15 P. M. There were 22 papers on the program, four of which were read by title, one by another member in the absence of its author, and 17 by their authors in the order as shown on the program. The attendance was 28 out of a membership of 76.

The following is a roster of the members of the Academy for 1913-14. The names of those in attendance at the meeting are marked with a star:

Addickes, T. W., Assistant Curator, State Museum, Raleigh.
Allen, W. M., State Feed Chemist, Department Agriculture, Raleigh.
*Balcomb, E. E., Professor of Agriculture, State Normal College, Greensboro.
*Binford, Raymond, Professor of Biology, Guilford College.
Blanchard, Julian, Professor Elect. Eng., Trinity College, Durham.
Booker, Warren H., Assistant Secretary State Board Health, Raleigh.
Boomhour, J. G., Professor Mathematics, Science, Meredith College, Raleigh.
Briggs, R. W., Professor Engineering, Trinity College, Durham.
*Brimley, C. S., Naturalist, Raleigh.
Brimley, H. H., Curator State Museum, Raleigh.
*Bruner, S. C., A and M. College, W. Raleigh.
Cain, William, Professor Mathematics, University of North Carolina, Chapel Hill.
Chrisman, W. G., State Veterinarian, Department Agriculture, Raleigh.
*Clapp, S. C., Orchard and Nursery Inspector, Department Agriculture, Raleigh.
Cobb, Collier, Professor of Geology, University of North Carolina, Chapel Hill.
Coker, R. E., Director U. S. Fisheries Station, Fairport, La.
*Coker, W. C., Prof. of Botany, Univ. of N. C., Chapel Hill.
Collett, R. W., Supt. State Exper. Farms, Swanannoa.
*Cunningham, Bert, Instructor in Sciences, High School, Durham.
*Dixon, A. A., Prof. of Physics, Guilford College.
*Downing, J. S., Prof. of Chemistry, Guilford College.
*Edwards, C. W., Prof. of Physics, Trinity College, Durham.
Ferrell, J. A., Assistant State Board Health, Raleigh.

Fulton, H. R., Professor Botany and Plant Pathology, A. and M. College, W. Raleigh.

*George, W. C., Instructor in Zoology, University of North Carolina, Chapel Hill.

*Gove, Anna M., Resident Physician, State Normal College, Greensboro.

*Gudger, E. W., Professor Biology and Geology, State Normal College, Greensboro.

*Hammel, W. C. A., Professor Physics and Manual Arts, State Normal College, Greensboro.

Harding, W. T., 116 W. Jones St., Raleigh.

*Herty, C. H., Professor of Chemistry, University of North Carolina, Chapel Hill.

Hobbs, A. Wilson, Graduate Student Johns Hopkins University, Baltimore.

Holmes, J. S., State Forester, Geology Survey, Chapel Hill.

*Hutt, W. N., State Horticulturist, Department Agriculture, Raleigh.

Ives, J. D., Assistant in Biology, Wake Forest College, Wake Forest.

*Julian, C. A., Assistant Secretary State Board Health, Thomasville.

Kilgore, B. W., State Chemist, Department Agriculture, Raleigh.

Lanneau, J. F., Professor Applied Math. and Astronomy, Wake Forest College, Wake Forest.

Lay, George W., Rector St. Mary's School, Raleigh.

Lewis, R. H., President North Carolina Association Prevent. Tuberculosis, Raleigh.

MacConnell, J. W., Professor Biology, Davidson College, Davidson.

McIver, Mrs. Chas. D., Spring Garden St., Greensboro.

MacNider, G M., Feed Chemist Department Agriculture, Raleigh.

MacNider, W. de B., Professor Pharmacology, University of North Carolina, Chapel Hill.

Markham, C. B., Assistant Professor Mathematics, Trinity College, Durham.

*Mendenhall, Gertrude W., Professor Mathematics, State Normal College, Greensboro.

*Metcalf, C. L., Entomologist, Department Agriculture, Raleigh.

*Metcalf, Z. P., Professor Entomologist, A. and M. College, W. Raleigh.

Mills, J. E., Consult. and Analyt. Chemist, Columbia, S. C.

Newman, C. L., Professor Agriculture, A. and M. College, W. Raleigh.

Norton, W. C., Asst. in Botany A. and M. College, W. Raleigh.

Patterson, A. H., Professor of Physics, University of North Carolina, Chapel Hill.

Pegram, W. H., Professor of Chemistry, Trinity College, Durham.

Petty, Mary M., Professor of Chemistry, State Normal College, Greensboro.

Poteat, W. L., President and Professor of Biology, Wake Forest College, Wake Forest.

*Pratt, J. H., State Geologist, Chapel Hill.

Radcliffe, Lewis, Director Laboratory U. S. Bureau Fisheries, Beaufort.

Ragsdale, Virginia, Associate Professor of Mathematics, State Normal College, Greensboro.

Rankin, W. S., Secretary State Board Health, Raleigh.

Robinson, Mary, Assistant in Biology State Normal College, Greensboro.

Rosenkrans, D. B., Instructor Botany, A. and M. College, W. Raleigh.

Shaw, S. B., Department Agriculture, Raleigh.

Sherman, Franklin Jr., State Entomologist, Department Agriculture, Raleigh.

Shore, C. A., Director State Laboratory Hygiene, Raleigh.

Smith, J. E., Instructor in Geology, University N. C., Chapel Hill.

Stiles, C. W., Director Marine Hospital, Wilmington.

*Strong, Cora, Associate Professor of Mathematics, State Normal College, Greensboro.

*Swarthout, G. E., Professor Nat. Science, Atlantic Christian College, Wilson.

Tillman, Opal I., Scientific Assistant Department Agriculture, Raleigh.

Venable, F. P., President University of N. C., Chapel Hill.

*Wheeler, A. S., Associate Professor Organic Chemistry, University N. C., Chapel Hill.

Williams, L. F., Associate Professor Chemistry, A. & M. College, W. Raleigh.

*Wilson, H. V., Professor Zoology, University of North Carolina, Chapel Hill.

Wilson, R. N., Professor Chemistry, Trinity College, Durham.

*Winters, R. Y., Plant Breeder, N. C. Agr. Experiment Station, W. Raleigh.

*Withers, W. A., Professor of Chemistry, A. & M. College, W. Raleigh.

*Wolfe, J. J., Professor of Biology and Geology, Trinity College, Durham.

In addition to the presidential address on "Zoo-geography," which is published in the current number of this JOURNAL, the following papers were presented:

WILL CELLS OF THE EMBRYO SEA URCHIN, WHEN REINTRODUCED INTO THE BODY OF THE ADULT, BECOME TISSUE CELLS OF THE LATTER

H. V. WILSON

Plasmodia formed by union of lymph cells were allowed to engulf blastulæ, and were grafted on the wound membranes which close in apertures made in the test of the urchin. The blastulæ after certain changes broke up into their constituent cells. In this way disssociated embryonic cells were brought into the midst of a developing membrane, having a very simple histological character. In the actual experiments a very large proportion of the embryonic cells underwent degeneration. There was some evidence, though by no means convincing, that groups of the smaller cells became part of the developing membrane.

ALTERNATION OF GENERATIONS IN PADINA

JAS. J. WOLFE

While at work on the life history of Padina at the Fisheries Laboratory at Beaufort it seemed worth while to test the theory of alternation of generations in such plants by the cultural methods devised by Hoyt (Bot. Gaz., Jan., 1910). Numerous cultures were made during the summer of 1910 and the next—all having but indifferent success. They were repeated in 1912 with somewhat better results. The cultures of Tetraspores produced a total of 134 male, 154 female, and no tetrasporic plants. Those from fertilized eggs were somewhat less conclusive. Nevertheless, the evidence from cultures strongly supports the view that in Padina there is a real alternation of sporophyte with gametophyte.

GESTATION IN THE NURSE SHARK, *GINGLYMOSTOMA CIRRATUM*

E. W. GUDGER

A brief description was given of the breeding habits and of some points in the embryology of this shark, which was studied at the laboratory of the Carnegie Institution at Tortugas, Florida, in June and July, 1912. A brief account has been published in the Year Book for 1912 of the Carnegie Institution of Washington, Department of Marine Biology, pages 148-150.

HYBRIDIZATION EXPERIMENTS ON FROGS

W. C. GEORGE

Chorophilus n. feriarum was crossed with Acris gryllus. About half of the egg segmented. (In the pure Chorophilus control practically all the eggs segmented). The development was markedly retarded and was abnormal. The conspicuous abnormalities concerned the behavior of the yolk pole. Thus segmentation at this pole was not perfect, and the closure of the blastopore was interferred with in such wise that there developed the well known abnormal type produced in so many ways, characterized by a large blastopore area and the differentiation of the neural plate.

THE TOXICITY OF COTTONSEED MEAL

W. A. WITHERS, J. F. BREWSTER, L. F. WILLIAMS, AND J. W. NOWELL
WITH THE COLLABORATION OF R. S. CURTIS AND G. A. ROBERTS

The authors conclude from experiments, some of which have been published:* that the toxicity of cottonseed meal is due to a constituent

Journal of Biological Chemitry, Volume XIV (1913), pp. 53-58.

group of the proteins, probably one containing loosely bound sulphur. They suggest some form of iron as an antidote having found with Belgian hares that citrate of iron and ammonia (0.7 gms. daily) is effective

*Proceedings Society for Promotion Agricultural Science, 1912, pp. 19-21,

in overcoming and in preventing cottonseed meal intoxication. Further experiments are in progress with small animals and with swine. Efforts to isolate the toxic substance will be continued.

FISHING FOR SHARKS IN KEY WEST HARBOR

E. W. GUDGER

In this paper the capture was described of a 7-foot, 10-inch male specimen of *Hypoprion brevirotris* and a 10-foot, 10-inch female specimen of the tiger shark, *Galeocerdo tigrinus*, in Key West Harbor, in July, 1912. These two fishes not being very well known, it is proposed later to publish careful descriptions with exact measurements.

The jaws of the tiger shark, which were exhibited, measured 1 foot 4 inches straight across, and around the curve of the jaws 1 foot 9 inches. Its stomach contained more than a half barrel of miscellaneous material, including a cow's head (dehorned) minus the lower jaws, the vertebral column of a sheep, the scutes of a green turtle, the bones and feathers of two birds, and a lot of tin cans and sea weed. The uteri were dissected, but unfortunately the fish was not in breeding condition.

A SECOND CAPTURE OF THE WHALE SHARK, *RHINEODON TYPUS*, IN FLORIA WATERS

E. W. GUDGER

This paper will be published in full in *Science*.

For the following papers no abstracts have been received:

Some Possible Effects of Solar Rays, (read by title), George W. Lay.
Seasonal Periodicity in the Water Moulds, W. C. Coker.
Vaccination Against Tuberculosis, C. A. Julian.
The Geological History of Western North Carolina, J. H. Pratt.
Action of Ammonia upon Arsenic Iodide, C. H. Herty, & J. T. Dobbins.
A List of the Known Homoptera in North Carolina, Z. P. Metcalf.
The Chestnut Bark Disease, S. C. Bruner.
Serum-Simultaneous Method of Immunizing Hogs Against Cholera. W. C. Chrisman.
Behavior of the Spermatozoa of the Crab, Raymond Binford.
The Granville Tobacco Wilt Problem, (read by S. C. Bruner), H. R. Fulton.
The Swamp Lands of Eastern North Carolina, J. H. Pratt.
The Influence of Environment on Reproductive Processes, W. C. Coker.
Survivals and Adaptions along the South Atlantic Coast: A Study in Anthropegeography, (read by title), Collier Cobb.
A New Interference Apparatus (with a demonstration), C. W. Edwards.
The Closing Up of Lake Basins in Massachusetts, Michigan, and North Carolina (read by title), Collier Cobb.

E. W. GUDGER, *Secretary.*

ZOO-GEOGRAPHY*

A Study of Life Zones

BY C. S. BRIMLEY

The intention of this paper is to discuss briefly, first, the primary life areas of the world, second, the life zones of North America, and thirdly the zoo-geographical divisions of our own state, North Carolina.

The primary life areas of the world appear to me to be five in number, namely:

An Australian Realm, consisting of Australia proper, New Guinea and the adjacent islands as far west as Celebes and Lombok. To these are also added New Zealand and the islands of Oceania.

A Neo-tropical Realm, comprising South America, Central America, the West Indies, and the coasts of Mexico.

An Ethiopian Realm, consisting of Africa south of the Sahara Desert, southern Arabia, and the island of Madagascar.

An Indian or Oriental Realm, including India, Further India, part of southern China, and the neighboring islands of the Malay Archipelago as far east as Borneo and Java.

A Northern Realm, comprising North America, Europe, northern and central Asia, and northern Africa, being equivalent to the combined Nearctic and Palæarctic Realms of Sclater and later writers.

This is practically the first system ever proposed, that of Sclater, 1858, with only one alteration, the combining of his Palaearctic and Neartic Realms into a single Northern Realm. Many systems have been suggested since, these consisting largely of different groupings of Sclater's original six realms, with or without the addition of certain others, constructed either of single islands as in the case of Madagascar, or of groups, as in the case of Oceania. The Arctic regions have also been set off as a distinct realm but this does not seem to be a tenable position as all the Arctic animals belong to families attaining their full development further south. An Antarctic realm has also

*Presidential address before the North Carolina Academy of Science, Greensboro, N. C., April 25, 1913.

been proposed but that would be characterised only by a single family of birds, the penguins, and it seems most advisable in this paper to look upon it as a region of secondary rank, or else to ignore it altogether. It seems to me also better to treat islands having a decidedly distinctive fauna as portions of the realm to which they most nearly approach, rather than to consider them as distinct, as there are all grades of such islands, and to recognize one opens the way to an almost endless list of meager insular realms.

In this paper the distribution of land vertebrates only will as a rule be taken into account, and greater weight will be given to the occurrence of mammals, reptiles, and amphibians, than to that of birds, as the latter, owing to their powers of flight and migratory habits are less reliable indications of the zoological character of a region than the former. Both fishes and birds will however be used whenever it seems advisable.

As the Northern Realm is distinguished from the group of four southern realms, more by the lack of the groups peculiar to them than by the presence of distinctive forms of its own, I will leave the discussion of its animals to the last, and take up the southern realms first, in the order in which they have been previously named. A further reason for this lies in the fact that after discussing the realms in general, I shall treat the life zones of North America, a portion of the Northern Realm, and this arrangement allows me to approach this second part of my subject in a natural and convenient way.

The Australian Realm comprises not only Australia, New Guinea, and the neighboring islands as far west as Celebes and Lombok, but also New Zealand and the islands of Oceania, which two last may be looked upon as outlying provinces and taken up later.

It is one of the most sharply characterised of the realms, its main features being the presence here, and here only, of the egg-laying mammalia, and the great development of marsupial mammals and elapid serpents to the exclusion of other forms of these groups, these being represented in Australia only by a few rodents and bats on the one hand and a few harmless snakes on

the other. Its marsupials and other distinctive forms become mingled with Asiatic species in the islands westward of New Guinea, but both marsupials and ostrich-like birds (which here attain their greatest development) extend up to and including the islands of Lombok and Celebes, but not across the straits to Borneo or Java. Side-necked turtles, and lung fishes are also represented here, as well as in the Neo-tropical and Ethiopian realms, but no cecilian amphibians.

New Zealand lacks most of the Australian forms, but is remarkable for the possession of the only living representative of the reptilian order Rhynchocephalia, while the islands of Oceania possess a fauna which, as we might naturally expect, is so largely composed of birds that they have sometimes been erected into a zoo-geographical realm under the name of Ornithogæa or the bird world.

The Neo-tropical Realm includes South and Central America, the coast lands of Mexico and also the West Indian islands. The presence of high mountains whose peaks reach above the snowline and the southward extension of the continent into cooler latitudes combined with tropical conditions over most of the realm make a homogeneous fauna impossible, still the whole realm shows marked distinctions from any other.

New-world monkeys, mormosets, sloths, ant-eaters, armadillos, and true opossums, the only family of pouched mammals found outside Australia, are all peculiar types characteristic of this realm only, while its rodent family Caviidæ contains the largest of all the order, one species, the capybara, reaching a weight of 100 pounds. Leaf-nosed or vampire bats are found exclusively here while the fruit bats of the other three southern realms are absent, as are also terrestrial insectivores. Hollow-horned ruminants are wholly absent, the hoofed mammals being represented by deer, tapirs, llamas, and peccaries.

Among birds members of the ostrich family occur, as well as many peculiar forms, such as the tinamous, toucans, and humming birds, the last being a highly characteristic and widespread family.

Crotalid, elapid, and boid snakes are represented in its fauna,

as well as side-necked turtles, lungfishes, and cecilian amphibians. Salamanders are practically absent.

The islands of the Greater Antilles deserve mention as lacking the terrestrial mammals of the neighboring mainlands, its only prominent forms being the rodent genus, Capromys, and the insectivorous genus Solenodon.

The Ethiopian Realm includes not only Africa south of the Sahara Desert, but also the island of Madagascar and southern Arabia. As the two latter, however, can only be considered as outlying provinces, and do not exhibit the more prominent features of the main portion of the realm they will be treated of separately, and are not included in the statements that immediately follow.

Its characteristic animals are the hippopotamus, giraffe, hyrax or coney, zebra, rhinoceros, elephant, old world monkeys, great apes (gorilla and chimpanzee), lemurs, scaly ant-eaters, aard vark, several families of insectivorous mammals (golden moles, jumping shrews, and some others), hyænas, ostrich-like birds, elapid, and boid snakes, side-necked turtles, cecilians or worm-like amphibians, and lung fishes. The greater number of these forms are represented in other realms as well, but the first four mentioned, as well as the aard vark, golden moles and jumping shrews do not occur elsewhere. No bears, deer, nor salamanders of any kind occur. Its main feature, however, is the great abundance of hoofed mammals, particularly those of the hollow-horned or antelope family which here attains by far its highest point, both in number of species and number of individuals.

Of its outlying portions the presence of conies and ostriches in southern Arabia would seem to indicate Ethiopian affinities, though most of the continental African forms are lacking.

The island of Madagascar on the other hand has a very peculiar fauna of its own, more than one-half of its mammals belonging to the lemur family, while the remainder are largely insectivora not found elsewhere, the large hoofed mammals, and the carnivora of the mainland being lacking.

The Indian or *Oriental Realm* comprises southeastern Asia,

south of the Himalaya Mountains, as well as the islands of the Malay Archipelago as far east as Borneo and Java.

It has been combined by some with the Palæarctic and Nearctic realms to form a single Arctogæan Realm, but it appears to me to have too many southern forms to justify such an arrangement, while others have combined it with the Ethiopian to form an Indo-African realm but here the lack of too many of the Ethiopian forms seems to be a sufficient bar to any such proceeding.

It possesses few peculiar groups of animals, the families Tupaiidæ (tree shrews), Galeopithecidæ (flying lemurs), and Tarsiidæ being the most noteworthy among the mammals, but the majority of its characteristic groups are shared with other realms, thus its elephants, hyænas, rhinoceros, scaly ant-eaters, lemurs, old world monkeys, and great apes are represented also in Africa, though by other species. Its boid snakes, and cecilian amphibians are similarly found also in both the Ethiopian and Neo-tropical realms. Its bear and deer and most of its insectivorous mammals are otherwise mainly northern groups, while it possesses in common with the Neo-tropical realm representatives of the tapir family. Lung fishes, side-necked turtles, and ostrich-like birds are absent, while elapid serpents are present, as they are also in all the other southern realms, being one of the very few groups found in all four tropical realms, and not elsewhere, the parrots being the only other vertebrate group which I can remember as having a similar range.

The *Northern Realm* comprises all the earth's land surface lying north of the boundaries of the four southern realms.

It is characterised more by what it lacks than by what it possesses, few groups of animals being confined exclusively within its borders.

No elephants, tapirs, rhinoceros, hippopatamus, giraffes, conies, no lemurs, monkeys of any kind, nor great apes, no edentates or marsupials, no egg-laying mammals, hyænas or cavies, no ostrich-like birds, no alligators, no boid nor elapid serpents, no side-necked turtles, no cecilian amphibians nor lung fishes occur, except that in the case of some of these groups a single species or two intrudes more or less into its limits.

Bears, deer, and insectivorous mammalia occur throughout practically its entire extent, tailed amphibians (salamanders) are found throughout its temperate regions and here alone.

It appears to me to fall into three natural divisions:—

1. *An Arctic Region,* comprising the circumpolar regions as far south as the northern limit of the growth of trees.

2. *An Eurasian Region,* (equivalent to Sclater's Palæarctic Realm, with its Arctic portion deducted), comprising Europe, north Africa, and Asia, north of the Indian Realm.

3. *A North American Region* (equivalent to Sclater's Nearctic Realm less Arctic North America), comprising all North America south of the Arctic regions and north of the Neo-tropical realm.

The *Arctic Region* is characterized by the scantiness of its fauna which is circumpolar for the most part, its most prominent mammalian components being the polar bear, Arctic fox, Arctic wolf, Arctic hares, reindeer, and musk ox, the last being American only.

The *Eurasian Region* possesses the following forms not found in North America, though mainly in other regions, in Insectivora, the hedgehogs, in Ungulata, the true oxen and buffaloes, the pigs, wild goats, and several species of antelopes. In reptiles it possesses true viperine serpents, and in birds, true flycatchers (Muscicapidæ), bustards (Otidæ), old-world warblers (Sylviidæ), true larks (Alaudidæ) and wagtails (Motacillidæ), the last three families being also very sparingly represented in America.

The *North American Region* lacks the above mentioned Eurasian forms and possesses the following peculiar ones: prong-horn antelope, skunks, o'possum, raccoon, star-nosed mole, mole shrews, and perhaps a few other mammals. Hoofed animals are comparatively poorly represented, there being, except the various deer, only the prong-horn, rocky mountain sheep, rocky mountain goat, and American bison, the last now nearly extinct. Among birds the wood warblers, tanagers, mocking thrushes, new world vultures, tyrant fly catchers and hummingbirds distinguish it from the Eurasian region, but all of them

occur more or less abundantly in the Neo-tropical realm to the southward. In reptiles it possesses pit vipers but no true vipers, and among the former the rattlesnakes are exclusively American and predominantly North American. In the Amphibia its characteristic species belong to the tailed forms among which the large family Plethodontidæ is exclusively North American while the smaller families of Sirenidæ, and Amphiumidæ containing the large eel-shaped salamanders are not found elsewhere.

THE LIFE ZONES OF NORTH AMERICA

These are more or less parallel belts running across the continent from east to west, and are limited mainly by the mean temperature of the region, which in its turn is determined by the two factors of latitude and elevation. Of course other factors play a large part in determining the life of these regions, the most important being the comparative humidity, in fact this last element splits three of our southerly life zones into two distinct portions, an eastern or humid division and a western or arid division.

These life zones are seven in number, the three northern being cold or boreal in character, while the four southern are warm or austral. Of course each zone grades into both the one above and the one below, so that there is never a hard and fast dividing line between any two contiguous ones, still in spite of this each zone is fairly well characterized by the forms of life or by the combination of forms occurring in it.

The transcontinental zones are,—

1. *An Arctic Zone,* forming the American portion of the Arctic region, including all the country north of the northern limit of trees.

2. *A Hudsonian Zone,* including the northern half of the boreal forest region.

3. *A Canadian Zone,* including the southern half of the boreal forests. These three zones cover by far the greater part of Canada and enter the United States, mainly along its chief mountain ranges at high elevations.

4. *An Alleghanian Zone,* which includes, roughly speaking, the northern United States.

5. *An Upper Austral Zone,* covering the middle portion of the United States, and divided into an eastern or humid portion (the Carolinian district), and a western or arid portion (Upper Sonoran).

6. *A Lower Austral Zone,* comprising the southern United States and the central plateau of Mexico, likewise divided into an eastern (Louisianian) or humid region, and a western (Lower Sonoran), or arid region.

7. *A Tropical Zone,* comprising all south of the Lower Austral.

The main characteristics of these zones are as follows:

1. *The Arctic Zone* is distinguished by an entire absence of trees, the vegetation consisting of stunted shrubs, low flowering plants, and lichens. Among the vertebrates, reptiles and amphibians are wholly lacking, while mammals are represented by the musk-ox, barren ground caribou, arctic hare, several species of lemmings, arctic fox, and near salt water and on the islands of the Arctic sea, by the polar bear. On the summits of the Rocky Mountains and of the Sierras where isolated patches of this zone occur at high altitudes these are all absent, but pikas, mountain sheep, and marmots occur at least in summer. Among the breeding birds of the Arctic zone are the snow geese and gyrfalcons and quite a number of shore birds. The mean temperature of the six warmest months at the lower edge of this zone is said to be about 50 F.

2. *The Hudsonian Zone* is a belt of more or less stunted timber lying due south of the preceding. Like it, it lacks all reptiles and amphibians, and also all the characteristic Arctic mammals as well, this being due not alone to the higher temperature but largely also to the forested character of the country, which prevents it being congenial to the animals which inhabit the treeless country further north. For the same reason the forest loving forms of the north, such as the wolverine, fisher, marten, Canada lynx, woodland caribou, moose, and black bear

do not range further northward. There seem to be no mammals peculiar to it and it is chiefly distinguished from the Canadian zone by what it lacks. Most of its characteristic mammals occur also on the isolated patches of it which lie on the sides of the western mountains below timber line. The mean temperature of the lower edge of this zone during the six warmest months in the year is said to be about 57 F. From its forested area, largely consisting of spruces, it is often known as the Spruce Zone.

3. *The Canadian Zone* includes the forested region consisting largely of balsams and firs which lies south of the Hudsonian, and does not differ from it greatly in character. It, however, is the most northern zone in which cultivated crops, such as potatoes, barley, etc., can be raised, and also is the most northerly zone in which any mammals of presumably southern origin occur. Thus chipmunks, white-footed mice and wood rats do not extend their range northward beyond it. Practically all the mammals mentioned above as belonging to the Hudsonian zone belong here also and these do not range southward below it (except the black bear). It possesses a few amphibians, such as frogs of the genus Rana, and salamanders of the genera Desmognathus and Amblystoma as well as a number of peculiar mountain forms. The temperature of the six warmest months of the year is estimated to be about 60 F.

4. *The Alleghanian Zone* includes the white pine forests of the north and the contiguous regions, and is the most northerly region having any reptilian fauna. The blue-tailed and fence lizards, the water, garter, chicken, ground, and green snakes as well as the copperhead, banded rattlesnake and massasauga do not extend north of it, nor in mammals do the cottontail rabbit, common mole, and raccoon, while the starnosed and Brewer's moles are confined to this zone and the Canadian. Salamanders attain their highest degree of development in this zone and the succeeding one.

5. *The Upper Austral Zone* is a tract of country in which the trees are mainly deciduous, thus forming a contrast to the coniferous forests of the north and south, between which it lies. Among mammals the gray fox, and opossum do not occur above

its northern boundary while the woodchuck, red fox, weasel, and chipmunk do not extend below its southern border. Its reptiles are much more numerous than those of the Alleghanian, but far less so than those of the Lower Austral. It divides naturally into an eastern or humid division and a western or arid one, the former being characterized by an abundance of turtles, and a scarcity of lizards while the latter has an abundance of lizards and very few turtles.

6. *The Lower Austral Zone* comprises roughly speaking the southern third of the United States and a large part of Mexico. It is characterized by a great abundance of reptiles and a comparative lack of salamanders though certain highly specialized forms of the latter belong exclusively here. Its distinctive mammals are the marsh and water rabbits, the cotton rats, and ricefield rats, and a few others. Its peculiar reptiles are many and will be mainly listed in the part on the life zones of North Carolina. The alligator, diamond rattlesnake, and coral snake are among its more striking representatives in the reptiles.

THE LIFE ZONES OF NORTH CAROLINA

Four of the life zones of North America enter the confines of our states, these are:

1. *The Canadian Zone.*
2. *The Alleghanian or Transition Zone.*
3. *The Upper Austral* or *Carolinian Zone.*
4. *The Lower Austral* or *Louisianian Zone.*

1. The Canadian Zone occupies the summits of the higher mountains from about 4,500 feet up, though some of its characteristic forms occur lower down still.

Its mammals are

Cloudland Deer Mouse, above 5,000 feet.
Carolina Red-backed Mouse, above 4,000 feet.

And there seem to be no other species of general distribution in the mountains which are confined to this zone, but its breeding birds are more distinctive, these being:

Pine Siskin, above 5,000 feet.
American Crossbill, above 5,000 feet.
Winter Wren, above 4,000 feet.
Brown Creeper, above 4,000 feet.
Redbreasted Nuthatch, above 5,000 feet.
Chickadee, above 5,000 feet.
Gold crowned Kinglet, above 5,000 feet.
Olive-sided Flycatcher, above 4,000 feet.
Yellow-bellied Sapsucker, above 4,000 feet.

The zone has not peculiar reptiles, those entering it, if any, being species occurring in the Alleghanian zone below. Its distinctive amphibians are also few, the most characteristic being *Plethodon metcalfi;* which however, ranges as far down as 3,500 feet, *Plethodon shermani* and *Gyrinophilus porphyriticus* also seem to belong to this zone, though the first seems to be a local form of very limited range, and of the latter we have only two records, one of them quite unsatisfactory.

The specific points which we are able to include in this zone from a more or less complete knowledge of their fauna are, the Black Mountains in Yancey and Buncombe Counties; Roan Mountain, in Mitchell County; Grandfather Mountain in Watauga County, Pisgah Ridge, and the Balsam Mountains in Haywood County, the high mountains near Highlands, in Macon County, Tuskwitty Mountain and Wayah Bald, also in Macon County. Besides these the mountains along the state line north of Cherokee County, as far as Roan Mountain, must possess a Canadian fauna on their summits owing to their elevation and the same is also true of all our mountains not named, which reach 5,000 feet elevation and over.

2. *The Alleghanian Zone* occupies the greater part of the mountain region, its limits extending from about 2,500 feet to 4,500 feet, though many of its characteristic species extend upwards into the Canadian, or downwards into the Upper Austral as well.

The following mammals do not appear to range below this zone: red squirrel, woodchuck, starnosed and Brewer's moles, mole-shrew, masked and smoky shrews, while the opossum,

woodchuck, gray squirrel, common deer mouse and common mole do not occur above it.

With birds the case is quite similar. The scarlet tanager, rosebreasted grosbeak, vesper sparrow, Carolina junco, song sparrow, Baltimore oriole, Cairns, Canadian, blackthroated green, blackburnian, golden-winged, and chestnut-sided warblers, Bewick's wren, warbling vireo, Wilson's thrush, least flycatcher and ruffed grouse not ranging below it, while the Carolina wren, crow, tufted tit, bluegray gnatcatcher, brown thrasher, yellowthroated vireo, Kentucky warbler, summer tanager, field sparrow, acadian flycatcher, and redbellied woodpecker do not pass beyond its upper limits. Not all of either class however ranges throughout its whole extent, a noteworthy exception being the Carolina junco, which is essentially a bird of the Canadian zone, but ranges in diminished numbers down to 3,000 feet, or about half way through the Alleghanian zone, and there are many similar instances.

In reptiles the milk snake alone appears to be confined to this zone, but the ring-necked snake, banded rattlesnake, garter snake, northern water snake, black chicken snake, black snake, fence lizard, blue-tailed lizard, and perhaps others also occur here as well as in the warmer zones below, and some of them may enter the Canadian zone above.

Its characteristic amphibians are wholly salamanders, the most widely distributed being the mountain triton (*Desmognathus 4-maculatus*) which occur in small streams throughout its whole extent. Another species is the round-tailed triton (*Desmognathus achrophea*) which though ranging in diminished numbers down to 3,000 ft. reaches its greatest abundance in the Canadian zone above. Daniel's triton (*Spelerpes danielsi*) and Schenck's triton (*Spelerpes schencki*), the former a rare, the latter a common, species seem to be confined to this zone. The viscid salamander extends upwards through this zone to about 3,500 ft. at which elevation it is replaced by Metcalf's salamander.

3. *The Upper Austral or Carolinian Zone.* This includes the central portion of the state, West and North of a line drawn

from a little West of Weldon, and thence through Raleigh to Charlotte. Its general western boundaries are the western limits of Surry, Wilkes, Caldwell, and Burke counties, some of all of which lie outside its limits. McDowell lies half in and half out of the zone, while Henderson is almost wholly outside and Polk almost wholly inside. Besides this it includes the mountain valleys below about 2,500 ft. the principal of them being those of the Hiwasee in Cherokee County, of the Little Tennessee in Graham, Swain, and Macon Counties, of Pigeon River in Haywood, and last but not least of the French Broad in Madison, Buncombe, Henderson, and Transylvania Counties.

Less collecting, especially if we exclude birds, has been done in our state in this zone than in any other, but fortunately what has been done has been largely near its edges and shows tolerably well how it differs from the zones above and below. Its faunal characteristics are furthermore much influenced by the comparative low latitude in which our portion of it lies so that we have an intrusion of certain Lower Austral forms and an exclusion of others which further north are characteristic of this zone.

We can define this zone but little by its mammalian fauna, still the golden mouse ranges throughout it but not above it, while the chipmunk, weasel, meadow mouse, jumping mouse, common deer mouse and muskrat, are also widely distributed forms whose range is largely defined by its southern border.

In birds the mocking bird, prairie warbler, pine warbler, yellowthroated warbler, blue grosbeak, brownheaded nut-hatch and Bachman's sparrow all occur more or less commonly up to its upper edge, the last four being normally Lower Austral species, while on the other hand the whippoorwill, robin, goldfinch, and yellow warbler do not range to any extent below its southern limits.

In reptiles it possesses one peculiar species, the brown king snake, a serpent of very limited distribution, but several do not range above it, these being the southern green snake, common king snake, Valeria's snake, ground lizard, and sand lizard. The black chicken snake, queen snake, and painted turtle do

not seem to extend their range much if any beyond its southern limits, while the northern water snake, although normally not occurring below this zone, ranges in this state throughout the Lower Austral also.

Among amphibians, the spotted salamander, marbled salamander and Holbrook's triton occur throughout it but not above its upper boundary, while the range of the pickerel frog does not extend below its southern limits.

From the Lower Austral it is mainly distinguished by the absence of the long list of reptiles and amphibians occurring in that zone and not above it. Some of these however enter the Upper Austral along its southern border, thus we have the green lizard recorded from Tryon in Polk County, and Albemarle in Stanley County, while the glass snake has been taken at Statesville. Other records of Lower Austral forms possibly still more surprising are of the lubber grasshopper near Concord in Cabarrus County, and a true scorpion at Tryon in Polk County.

4. *Lower Austral Zone,* includes the remainder of the state, namely all lying south and east of a line drawn from near Weldon to Raleigh, and thence to Charlotte, and it may be as well to give some idea of how we came to locate the line. In the first place, Raleigh, where the fauna is known in its entirety for all practical purposes, has a thoroughly mixed fauna and can hardly be placed in either zone, thus both the whippoorwill and chuckwillswidow, one typically Upper, and the other typically Lower Austral, both occur and breed. Other Upper Austral breeding birds are the robin, goldfinch, mountain vireo, and yellow warbler, while the prothonotary warbler, a Lower Austral form, barely reaches Raleigh. In reptiles we have here the following Upper Austral species: brown king snake, queen snake, black chicken snake, northern water snake, and painted terrapin, and these Lower Austral forms: glass snake, corn snake, southern water snake, cottonmouth, red-bellied water snake, crowned tantilla, red king snake, scarlet snake, and two species of terrapin (*Pseudemys concinna* and *P. scripta*). In amphibians the balance also turns to the Lower

Austral as the ditch eel (*Amphiuma means*), dwarf salamander and narrow-mouthed toad are all common, while the Upper Austral pickerel frog is only tolerably so. In mammals its Lower Austral forms are the cotton rat and Carolina mole-shrew, both of which may very likely range considerably into the Upper Austral in this state, while of Upper Austral forms, the chipmunk is common a few miles west of Raleigh, but not at Raleigh, while the meadow mouse, common deer mouse, muskrat, jumping mouse and weasel are all common except the last two.

Hence we see Raleigh rather leans to the Upper Austral on birds and mammals, and to the Lower on reptiles and amphibians, and is plainly an intermediate point so we draw the line right through it, then knowing that the line must necessarily slant northward towards the coast, we draw it straight to Weldon, having records of the occurrence of typical Lower Austral forms just east of that place. To the south we find that Southern Pines with records of the scarlet snake, coachwhip, corn snake, narrowmouthed toad, crowned tantilla, and red-cockaded woodpecker ought to be placed well within the line, which is confirmed by the occurrence of the green lizard at Carthage a little to the north, and of the coral snake at Montrose to the south. So we draw the line above Southern Pines, and then finding records of such species as the green lizard in Stanly County, and the lubber grasshopper in Cabarrus County which latter record is offset by the presence of the chipmunk, at the same place, indicating a mixed fauna, we continue it through these counties to Charlotte and thence to the state line in the same general direction.

The animals which we have considered as characterising the Lower Austral Zone in this state are as follows:

1. Mammals
   - Marsh Rabbit (Lepus palustris).
   - Southern Fox Squirrel.
   - Cotton Rat (Sigmodon hispidus).
   - Ricefield Rat (Oryzomys palustris).
   - Cotton Mouse (Peromyscus gossypinus).

Carolina Mole Shrew (Blarina carolinensis).
Southern Shrew (Sorex longirostris).
Big-eared Bat (Corinorhinus macrotis).

2. Birds (occurrence in the breeding season only taken into consideration).*

a Land Species.
Chuck-wills-widow.
Red-cockaded Woodpecker.
Prothonotary Warbler.
Swainsons Warbler.
Nonpareil or Painted Bunting.

b Shore and Water Birds.
American Egret.
Snowy Egret.
Florida Cormorant.
Louisiana Heron.
Little Blue Heron.
Boat-tailed Grackle.

3. Reptiles.

Alligator (Alligator mississippiensis).
Florida Terrapin (Pseudemys floridana).
Mobile Terrapin (Pseudemys mobilensis).
Yellow-bellied Terrapin (Pseudemys scripta).
Smooth Terrapin (Pseudemys concinna).
Diamond Rattlesnake (Crotalus adamanteus).
Ground Rattlesnake (Sistrurus miliarius).
Cottonmouth Mocassin (Ancistrodon piscivorus).
Coral Adder (Elaps fulvius).
Crowned Tantilla (Tantilla coronata).
Rainbow Snake (Abastor erythrogrammus).
Horn Snake (Farancia abacura).
Southern Hog-nosed Snake (Heterodon simus).
Striped Chicken Snake (Coluber quadrivittatus).

*The following birds usuallly considered as typically Lower Austral forms range in this state throughout the Upper Austral also and help to define it as opposed to the next more northern zone, the Alleghanian: blue grosbeak, Bachman's sparrow, brown-headed nuthatch and yellow-throated warbler.

Corn Snake (Coluber guttatus).
Red King Snake (Ophibolus doliatus cocoineus).
Scarlet Snake (Cemophora coccinea).
Pied Water Snake (Natrix taxispilota).
Southern Water Snake (Natrix fasciata fasciata).
Red-bellied Water Snake (Natrix fasciata erythrogastra).
Coachwhip (Bascanium flagellum).
Brown-headed Snake (Rhadinaea flavilata).
Glass Snake (Ophisaurus ventralis).
Green Lizard (Anolis carolinensis).

4. Amphibians.
Mud Eel (Siren lacertina).
Southern Water Dog (Necturus punctatus).
Ditch Eel (Amphiuma means).
Dwarf Salamander (Manculus quadridigitatus).
Margined Salamander (Stereochilus marginatus).
Narrow-mouthed Toad (Engystoma carolinense).
Dwarf Toad (Bufo quercicus).
Pine-woods Tree Frog (Hyla femoralis).
Squirrel Tree Frog (Hyla squirrella).
Carolina Tree Frog (Hyla cinerea).

5. Fish.
A Top Minnow (Heterandria formoso).
Ditch Fish (Chologaster cornutus).
Everglade Perch (Elassoma evergladei).
Swamp Darter (Copelandellus quiescens).

Not all of these species range throughout the whole zone, a great many of them not appearing to occur further north than Neuse River, while others again seem to be confined to the coastal region though ranging throughout the whole extent of that, in fact, there are all sorts of irregularities in the distribution of these species. Those confined to the coastal region are the following: rainbow snake, horn snake, striped chicken snake, diamond rattlesnake, pied water snake, mud eel, all the three tree frogs mentioned, all four fishes, probably the cotton mouse, and the water and shore birds mentioned. Those ap-

parently extending their ranges north of Neuse River are coachwhip snake, ground and diamond rattlesnakes, nonpareil, Florida cormorant, coral snake, and some others, but our data with regard to many of the species is so meager that we cannot draw any definite conclusions from it.

In part of the zone lying north of Neuse River there appears to be a much greater admixture of Upper Austral forms than further south; in fact, south of that line we meet with only scattering examples of species belonging to the more northern zone. Thus the localities lying on or above Neuse River (excluding Raleigh) give a total of 49 Lower Austral records, to 18 Upper Austral, while those localities southward give only 5 Upper Austral records to a total of 95 Lower Austral, thus showing a much greater intermingling as we go northward which is just what we ought to expect, as no life area is ever homogenous, but gradually blends on the borders with the adjoining ones or areas, consequently the boundaries we draw between any two contiguous zones are largely arbitrary, and if we drew maps to record things exactly as they are we would cause the colors of adjoining zones to gradually blend the one into the other just as their fauna actually blends.

RALEIGH, N. C.

METHODS FOR THE PREPARATION OF NEUTRAL SOLUTIONS OF AMMONIUM CITRATE[1]

BY JAMES M. BELL AND CHARLES F. COWELL

The method at present approved by the Association of Official Agricultural Chemists[2] for the preparation of neutral solutions of ammonium citrate requires the use of an alcoholic solution of corallin as indicator. It is common knowledge that this method is not accurate. The method proposed by Hand,[3] using purified litmus solution, has been thoroughly tried by Patten and Robinson[4] and like the corallin method has proven much less satisfactory than the conductivity method proposed by Hall and Bell.[5] By this conductivity method a series of solutions is prepared containing constant quantities of citric acid and variable quantities of ammonia in a constant volume. It was found that the solution just neutral has the highest electrical conductivity, the plot for conductivity and quantity of ammonia consisting of two curves intersecting at the neutral point. Up to that point the solutions consist of mixtures of ammonium citrate and free citric acid, and beyond the break the solutions consist of mixtures of ammonium citrate and free ammonia.

The conductivity method requires some temperature control, for the temperature coefficient of conductivity is large enough to cause serious errors in the final result unless the maximum variations in temperature are but very slight. Two further methods are here presented for the determination of the neutral point, neither of which requires careful temperature regulation. In one method there is an indirect determination of the excess of ammonia just past the neutral point by the use of chloroform as solvent. This method is called the "extraction method." The second method like the conductivity method is a physical method depending on the great heat evolution when ammonia and citric acid solutions are mixed. This has been called the "temperature method."

[1]Reprinted from The Journal of the American Chemical Society, Vol. XXXV. No. 1. January, 1913.
[2]Bureau of Chemistry, *Bull.* 107 (revised), 1.
[3]Bureau of Chemistry, *Bull.* 132, 11.
[4]*J. Ind. Eng. Chem.*, 4, 443 (1912).
[5]*J. Am. Chem. Soc.*, 33, 711. (1911.)

1. *Extraction Method.*—Ammonia is soluble to a slight extent in chloroform; citric acid and ammonium citrate are insoluble in chloroform. This fact affords an accurate method of estimating the excess of ammonia in an aqueous solution of these substances. The distribution ratio of ammonia between chloroform and water has been shown by Bell and Feild[6] to be about 1:25 at ordinary temperatures; that is, between equal volumes of water and chloroform, free ammonia will distribute itself about $^{1}/_{26}$ in the chloroform layer and $^{25}/_{26}$ in the water layer.

A citric acid solution containing 370 grams per liter was prepared. To 100 cc. lots of this solution varying amounts of strong ammonia were added and the resulting solutions diluted to 200cc. This addition was made through a narrow tube leading into the acid so as to avoid losses of ammonia by volatilization. Of this solution 100cc. were shaken out with 125cc. of chloroform and 50cc. of this chloroform layer to which about 50cc. of water were added was titrated against 0.1 *N* hydrochloric acid solution using methyl red as indicator. During this titration all the ammonia passed from the chloroform layer to the water layer as it was neutralized by the acid. In these determinations only a part of the total excess of ammonia is estimated, but knowing what fraction is taken, the total excess of ammonia may be estimated. For each gram of free ammonia left in 100 cc. of the water layer after shaking out, there is 0.04 gram in 100 cc. of the chloroform layer or 0.05 gram in 125 cc. of the chloroform layer. Hence, of the total excess of ammonia in the sample $^{1}/_{21}$ is in the 125 cc. of chloroform. In 50 cc. there are $^{2}/_{105}$ of the portion shaken out and as only half of the total is shaken out there is $^{1}/_{105}$ of the total excess of ammonia actually titrated.

TABLE I

Ammonia solution used.	0.1 N HCl required to neutralize 50 cc. chloroform extract.
Cc.	Cc.
40.5	1.50
40.2	0.97
40.0	0.47
39.8	0.22
39.5	0.00

[6] *J. Am. Chem. Soc.*, 33, 940 (1911).

The proportion in which the citric acid and ammonia solutions must be mixed to give a solution exactly neutral may be found by a graphic method. In Fig. 1 the number of cc. of ammonia added is abscissa and the number of cc. of acid required to neutralize the excess of ammonia in 50 cc. of the chloroform layer is ordinate. By extrapolating it is seen that 39.7 cc. of ammonia solution would just neutralize the amount of the citric acid solution employed. No trace of free ammonia was found in any of the solutions to which 39.5 cc. or less of the ammonia solution had been added. When as much as 40.0 cc. had been added, the free ammonia could be detected by odor and these solutions showed increasing amounts of ammonia in the titrations. The solution containing 39.8 cc. of ammonia contained very little free ammonia, for 50 cc. of the chloroform extract required only 0.22 cc. of the acid. It will be seen that this method will indicate the proportions in which the solutions of ammonia and citric acid must be mixed with at least the accuracy which is possible in the ordinary comparison of an acid and base by buret readings.

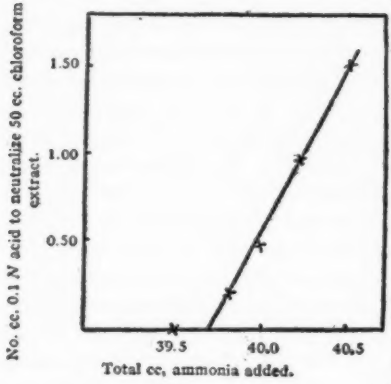

Fig. 1.

II. Temperature Method.—The second method here presented for the preparation of a neutral solution of ammonium citrate, like the conductivity method, is a physical method. It was suggested by the fact that, during the addition of the first 35 cc. of ammonia to the citric acid in the former method, so much heat was developed that the solution had to be cooled at least twice during the mixing. After the neutral point is reached, there is no appreciable heat effect due to further additions of ammonia.

The experiments were carried out in a Dewar flask of about 200 cc. capacity, provided with a platinum stirrer and a thermometer graduated to tenths of degrees. The citric acid and ammonia solutions were the same as those used in the former method. Again, 100 cc. of citric acid solution was partially neutralized with 36 cc. of ammonia solution in an ordinary beaker. The cooled solution was then poured into the Dewar flask. The beaker was washed several times with water and the washings poured into the Dewar flask, so that the final volume of solution was about 150 cc. Just as in the previous

TABLE II

Total ammonia added. Cc.	Temperature.
36.0	21.50°
36.5	21.88
37.0	22.25
37.5	22.62
38.0	23.04
38.5	23.40
39.0	23.70
39.5	24.12
40.0	24.28
40.5	24.30
41.0	24.30
42.0	24.32
45.0	24.32

method, the ammonia solution was added from a buret provided with a small delivery tube, which extended to the bottom of the flask. Ammonia was now added in portions of 0.5 cc. and the mixture stirred for about ½ minute. After 1½ minutes no further rise of temperature was noticed. After each addition of 0.5 cc. of ammonia there was a constant rise of temperature of about 0.40° until the buret reading was 39.50 cc. of ammonia. For the next 0.5 cc. of ammonia the rise of temperature was only 0.16°. Beyond 40 cc. practically no change in temperature occurred. The neutral point is therefore between 39.5 cc. and 40 cc. of ammonia. The exact neutral point is found by plotting the curve, using the number of cc. of ammonia as abscissa and the

rise of temperature as ordinate. This point is found to be 39.7 cc., the same reading as was found by the extraction method.

The "temperature method" was further confirmed by its use with solutions of sulphuric acid and ammonia, both about twice normal. The rise of temperature, taken with the same thermo-

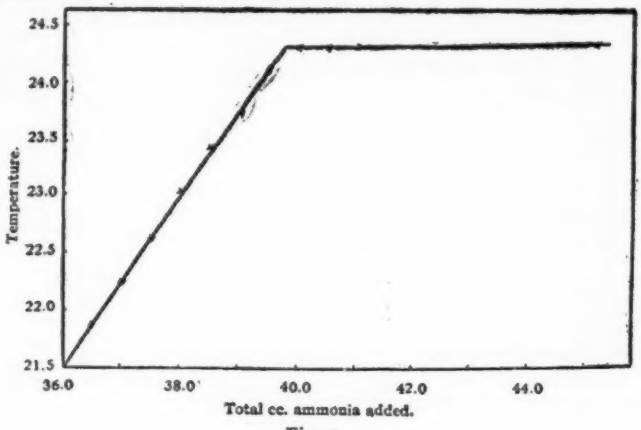

Fig. 2.

meter, as before, was constant until the neutral point was reached. The results obtained are given in Table III and the neutral point agrees exactly with that found by the direct titration of the ammonia against the acid.

TABLE III

Cc. Ammonia added to 40 cc. acid.	Temperature.
38.5	27.62°
39.0	27.70
39.5	27.79
40.0	27.88
40.5	27.96
40.1	28.05
41.5	28.05
42.0	28.01
42.5	27.98
43.0	27.95

Both methods here presented are for the determination of the proportion in which ammonia and citric acid must be mixed to arrive at a neutral solution. These proportions vary of course with the strength of the separate solutions. From the proportion found large quantities of neutral ammonia citrate may be prepared, after which the solution may be diluted to the required density.

SUMMARY

In this paper two methods are proposed for the determination of the end point in the titration of a weak acid by a weak base, where the ordinary indicators fail. In the first method an index of the excess of ammonia is obtained by shaking out with chloroform and by titrating the chloroform with a dilute acid. In the second method the rise in temperature due to the heat of neutralization is observed as the titration proceeds, the end point being at the break in the heating curve. Both these methods are simpler than the method formerly proposed where the conductivities of solutions must be determined at constant temperature.

CHAPEL HILL, N. C.